LES SPECTRES D'ABSORPTION DES COMPOSÉS AZOÏQUES MIXTES ET CEUX DE LEURS ISOMÈRES.[1]

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Un des auteurs du présent travail a déjà étudié[2] une quarantaine de composés oxyazoïques au moyen de leurs spectres d'absorption et a discuté leurs constitution chimiques en leur appliquant les courbes Hartley et Baly. Il y a encore ajouté des recherches plus détaillées[3] sur leur absorption ultra-violette en vue de déterminer leur structure moléculaire en solution aqueuse, en faisant varier leur concentration des ions d'hydrogène d'un certain nombre de ces composés.

Le mémoire actuel a une certaine relation avec nos recherches antérieures. On a pris la photographie des spectres d'absorption en se servant du spectrographe en quartz de l'Anglais Adam Hilger et étudié les bandes d'absorption dans les photographies prises. Nous avons, cependant, préparé des échantillons des substances azoïques mixtes (gemischte Azokörper[4]) et leurs isomères, afin d'observer les relations qui peuvent exister entre les chromophores contenus dans ces matières colorantes azoïques et leurs spectres d'absorption.

Procédé expérimental et préparation des corps étudiés. Le spectre d'absorption présenté dans le mémoire actuel a été pris par la méthode appliquée pour la première fois par Hartley et Baly (courbes Hartley-Baly), c'est-à-dire les logarithmes des épaisseurs des solutions liquides correspandant à la concentration de 1/10000 mol en axe des ordonnées dans les courbes, et la réciproque d'une longueur d'onde (la fréquence) en abcisse. Les photographies ont été prises sur une plaque orthochromique "Tôyô" (marque japonaise) par le spectrographe anglais ci-dessus décrit. La source lumineuse a été fournie par le courant continu (4 à 5 ampères à 100 volts) d'un arc métallique en fer. On a compté 15 secondes en moyenne comme temps de pose photographique et pris

(1) Traduit de la publication originale publiée dans le Bulletin de Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku Gakuhô), **3** (1934), 467. Exposé fait lors de la Séance de la Société chimique du Japon, le 14 juillet 1934.

(2) Ce bulletin, **1** (1926), 290; **2** (1927), 10, 48, 229, 249; **3** (1928), 105.

(3) *Arch. phys. biol.*, **9** (1931), 29; *J. Chem. Soc. Japan*, **54** (1933), 265.

(4) Radical azoïque lié d'une part par un aryle, et de l'autre par un alcoyle.

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l'alcool absolu comme dissolvant des corps étudiés. Les solutions alcooliques ont été obtenues en dissolvant l'échantillon purifié en fiole graduée. On en a préparé plusieurs espèces de concentrations des solutions: 1/10, 1/100 ou 1/10000 mol pour les utiliser convenablement.

On a préparé les 21 corps suivants par synthèse chimique, excepté l'azobenzène et la diphénylamine qui ont été obtenus l'un et l'autre dans le commerce.

(1) *Azobenzène,* $C_6H_5 \cdot N:N \cdot C_6H_5$. L'échantillon d'azobenzène utilisé par nous est produit par la compagnie Kahlbaum (marque allemande). C'est un cristal jaune-orange qui fond à 68°C.

(2) *Phénylazométhane,* $C_6H_5 \cdot N:N \cdot CH_3$. Le phénylazométhane qui a été préparé par Baly et Tuck[5] en faisant réagir la phénylhydrazine sur le formaldéhyde qui a été déjà examiné par Stobbe et Nowak[6], et ils le signalaient comme un produit impur. Nous avons donc adopté la méthode proposée par Tafel[7], c'est-à-dire méthyliser, saponifier la dibenzoylphénylhydrazine et l'oxyder par l'action de l'oxyde de mercure. Le composé ainsi obtenu est un corps jaune et huileux qui a une odeur spéciale et bout entre 52 et 54°C. sous 11 mm. de basse pression.

(3) *Phénylazoéthane,* $C_6H_5 \cdot N:N \cdot C_2H_5$. Ce corps synthétiquement formé d'après la méthode proposée par Fischer[8] est jaune et huileux avec une odeur caractéristique. Nous l'avons purifié par la distillation à vide deux fois répétée. Le composé ainsi obtenu bout entre 62 et 65°C. sous une pression de 10 à 12 mm.

(4) *Phénylazopropane,* $C_6H_5 \cdot N:N \cdot C_3H_7$. Suivant le procédé employé par Fischer[9] pour opérer la synthèse du phénylazoéthane et du phénylazopropène, on a fait réagir la phénylhydrazine en présence de l'éther sur le bromure de propyle pendant 30 heures, à la température ordinaire, et le résultat n'a pas été défavorable. On a dosé 15 g. de phénylhydrazine pour y ajouter 30 c.c. d'éther, et on a laissé reposer le mélange pendant 30 heures après l'avoir fait réagir sur 7 g. de bromure de propyle à la température ordinaire. Nous filtrons la phénylhydrazine ainsi précipitée et obtenons un sel incolore, puis nous faisons évaporer l'éther qui se trouve dans le filter, et nous éliminons la phénylhydrazine non réagie comme le hydrochlorate par le moyen de l'acide hydrochlorique concentré, puis nous neutralisons l'eau mère par la soude caustique pour

(5) E. C. C. Baly et W. B. Tuck, *J. Chem. Soc.*, **89** (1906), 986.
(6) H. Stobbe et R. Nowak, *Ber.*, **47** (1914), 578.
(7) J. Tafel, *Ber.*, **18** (1885), 1742.
(8) E. Fischer, *Ber.*, **29** (1896), 793.
(9) E. Fischer et O. Knoevenagel, *Ann.*, **239** (1887), 203.

obtenir le produit huileux jaune-brun dans l'éther. Cette solution éthérique est oxydée par l'action de l'oxyde de mercure et séchée par le carbonate de potasse. Nous procédons alors à une distillation à vide et nous obtenons une substance huileuse jaune qui bout à 85°C. sous une pression de 20 mm. Son rendement est de 0.5 g., et l'analyse chimique montre 0.513 c.c. (23°C., 760 mm.) d'azote de 3.074 mg. de l'échantillon; cela correspond à 19.03%, tandis que la valeur calculée est de 18.92%.

(5) *Phénylazobutane*, $C_6H_5{\cdot}N{:}N{\cdot}C_4H_9$. Nous avons synthétisé ce corps par une méthode semblable à celle qui a été appliquée au composé précédent.

Ayant pris 50 g. de phénylhydrazine, nous y ajoutons 100 c.c. d'éther et 25 g. de bromure de butyle. Nous laissons reposer le mélange pendant 30 heures à la température ordinaire, puis nous filtrons le sel incolore de phénylhydrazine ainsi cristallisé et après, nous éliminons la phénylhydrazine non attaquée par l'action de l'acide chlorhydrique concentré; nous neutralisons la solution éthérique au moyen de l'oxyde de mercure, nous séchons le tout avec le carbonate de potasse et distillons à vide pour obtenir un produit huileux, d'un jaune citron. Son rendement est de 1.1 g. et son point d'ébullition indique 90°C. sous pression réduite (19 mm.). L'analyse chimique révèle la présence de 0.677 c.c. (24°C., 757 mm.) d'azote sur 4.402 mg. de substance; cela correspond à 17.42%, tandis que la valeur calculée est de 17.28%.

(6) *Phénylazophénylméthane*, $C_6H_5{\cdot}N{:}N{\cdot}CH_2{\cdot}C_6H_5$. Nous avons préparé ce corps suivant les indications fournies par Thiele[10] et le produit jaune et huileux a une odeur caractéristique.

(7) *ω-Azotoluène*, $C_6H_5{\cdot}CH_2{\cdot}N{:}N{\cdot}CH_2{\cdot}C_6H_5$. La benzalazine est réduite par l'amalgame de sodium en solution alcoolique,[11] et, d'après la méthode de Thiele,[12] en l'oxydant avec l'eau oxygénée, on peut obtenir l'ω-azotoluène, cristal incolore, ayant son point de fusion à 31.5°C.

(8) *Formaldéhydephénylhydrazone*, $C_6H_5{\cdot}NH{\cdot}N{:}CH_2$. Ce composé a été synthétiquement obtenu, d'après les indications de Walker,[13] en présence de l'acide acétique. Lorsque deux mols de phénylhydrazine réagissent sur la solution aqueuse d'une mol d'aldéhyde formique, on obtient, mais non sans peine, un corps ayant son point de fusion à 155°C. Nous avons cependant réussi à stabiliser le corps au point de fusion ci-dessus nommé après les trois essais d'expériences, et le produit a été

(10) J. Thiele, *Ann.*, **376** (1910), 267.
(11) Th. Curtius, *J. prakt. Chem.*, **62** (1900), 90.
(12) J. Thiele, *Ann.*, **376** (1910), 265.
(13) J. W. Walker, *J. Chem. Soc.*, **69** (1896), 1282.

recristallisé dans le benzène. Comme ce composé est peu soluble dans l'alcool, sa photographie d'absorption n'a été prise qu'en utilisant sa solution à 1/10000 mol. Nous avons mis le reste du corps étudié dans le dessicateur pendant deux ou trois jours et avons observé qu'une transformation s'opérait dans cette substance et que son point de fusion s'élevait à 183°C. Nous avons encore des doutes sur l'existence de ce corps à l'état pur, non polymérisé, même du point de vue du spectre d'absorption.

(9) *Acétaldéhydephénylhydrazone*, $C_6H_5{\cdot}NH{\cdot}N{:}CH{\cdot}CH_3$. La substance obtenue d'après le procédé de Lockemann et de Liesche[14] se liquéfie entre 98 et 101°C. C'est un cristal incolore qui correspond au type *a* nommé par Fischer[15].

(10) *Propylaldéhydephénylhydrazone*, $C_6H_5{\cdot}NH{\cdot}N{:}CH{\cdot}C_2H_5$. D' après la méthode de préparation employée par Fischer,[16] on a fait réagir dans l'éther la phénylhydrazine sur l'aldéhyde propylique en quantités égales, on a éliminé l'eau qui s'est produite, on a desséché le corps par le carbonate de potasse et on l'a distillé sous pression réduite. Le produit ainsi obtenu qui bout à 135°C. sous la pression 18 mm. a une apparence huileuse.

(11) *Butylaldéhydephénylhydrazone*, $C_6H_5{\cdot}NH{\cdot}N{:}CH{\cdot}C_3H_7$. Ce corps a été préparé d'après la même méthode que les composés précédents, et suivant les indications données par Brunner;[17] c'est-à-dire qu'on fait réagir, en présence de l'éther, la phénylhydrazine sur l'aldéhyde normal-butylique prises l'une et l'autre en quantités égales, puis on en élimine l'eau et on dessèche au moyen du carbonate de potasse, puis on distille sous pression réduite. Le produit huileux ainsi obtenu a son point d'ébullition entre 141 et 143°C. sous 15 mm. de pression réduite, exposé à la lumière solaire, il devient jaunâtre.

(12) *Propanonephénylhydrazone*, $C_6H_5{\cdot}NH{\cdot}N{:}C(CH_3)_2$. Appliquant la méthode indiquée par Fischer,[18] nous ajoutons de la phénylhydrazone à l'excès d'acétone, nous éliminons l'eau qui s'est produite, puis nous desséchons au moyen du carbonate de potasse. Le corps obtenu par distillation sous pression réduite est une substance incolore et huileuse qui a son point d'ébullition à 135°C., sous 27 mm. de pression et qui devient jaune sous l'action de la lumière solaire.

(13) *Butanonephénylhydrazone*, $C_6H_5{\cdot}NH{\cdot}N{:}C(CH_3){\cdot}C_2H_5$. Ce corps s'obtient par la méthode de préparation proposée par Arbusow et

(14) G. Lockemann et O. Liesche, *Ann.*, **342** (1905), 14.
(15) E. Fischer, *Ber.*, **29** (1896), 795.
(16) E. Fischer, *Ann.*, **236** (1886), 137.
(17) K. Brunner, *Monatsh.*, **16** (1895), 184.
(18) E. Fischer, *Ann.*, **236** (1886), 126.

Tichwinsky,[19] mais il peut se former également en partant de la phénylhydrazine et de la méthyléthylcétone, qui entrent en quantités égales, et sont traités dans l'éther. On élimine l'eau qui s'est produite, on dessèche avec le carbonate de potasse et on fait la distillation sous pression réduite. Le composé ainsi obtenu est huileux et incolore, il bout à 140°C., sous 15 mm. de pression et devient jaunâtre sous l'action de lumière.

(14) *Benzaldéhydephénylhydrazone,* $C_6H_5{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_5$. La préparation de ce corps a été faite d'après les indications de Biltz,[20] et le produit ainsi obtenu, le soi-disant type *a* de Biltz, se présente sous l'aspect d'un cristal incolore ayant son point de fusion à 155°C. Il devient jaune sous l'action de la lumière.

(15) *Benzalbenzylhydrazone,* $C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_5$. Ce corps fut confondu d'abord par Curtius et Quedenfeldt[21] avec la benzylhydrazine symétrique. Nous l'avons cependant préparé suivant les procédés indiqués par Curtius[22], en employant la benzalazine réduite par l'amalgame de sodium. Le produit obtenu est un cristal incolore, qui a son point de fusion à 65°C.

(16) *Diazoaminobenzène,* $C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5$. Ce composé se forme d'après la méthode indiquée par Griess.[23] Le corps ainsi obtenu est un cristal jaune qui a son point de fusion à 96°C.

(17) *Diméthyldiphényltétrazone,* $C_6H_5{\cdot}N(CH_3){\cdot}N{:}N{\cdot}N(CH_3){\cdot}C_6H_5$. Suivant la méthode de synthèse de la diéthyldiphényltétrazone indiquée par Fischer,[24] une légère quantité de phénylhydrazone réagissant sur l'iodure de méthyle donne un cristal incolore qui a son point de fusion à 137°C.

(18) *Hydrazobenzène,* $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. Ce corps s'obtient, d'après les indications de l'ouvrage écrit par Vanino,[25] par la réduction basique de l'azobenzène en solution alcoolique sous l'action du zinc.

(19) *Diphénylamine,* $C_6H_5{\cdot}NH{\cdot}C_6H_5$. Le produit chimique fabriqué par Kahlbaum (marque allemande) est un cristal incolore qui a son point de fusion à 54°C.

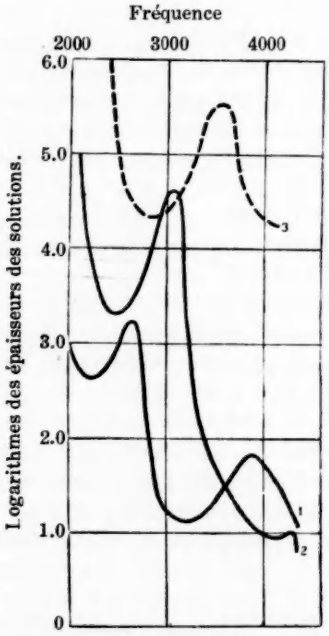
(20) *Benzalazine,* $C_6H_5{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}C_6H_5$. D'après la méthode indiquée par Curtius et Jay,[26] par l'action d'aldéhyde benzoïque sur la

(19) A. E. Arbusow et W. M. Tichwinsky, *Ber.*, **43** (1910), 2301.
(20) H. Biltz, *Ann.*, **305** (1899), 170.
(21) Th. Curtius et E. Quedenfeldt, *J. prakt. Chem.*, **58** (1898), 374.
(22) Th. Curtius, *J. prakt. Chem.*, **62** (1900), 90.
(23) P. Griess, *Ann.*, **121** (1862), 257.
(24) E. Fischer, *Ann.*, **190** (1877), 169; *Ber.*, **29** (1896), 793.
(25) L. Vanino, "Präparative Chemie", II (1923), 505.
(26) Th. Curtius et R. Jay, *J. prakt. Chem.*, **39** (1889), 27.

solution de hydrazine, on a un produit insoluble dans l'eau. Ce qu'on obtient par recristallisation dans l'alcool est un cristal jaune présentant la forme d'aiguilles et qui fond à 93°C.

(21) *Benzalaniline*, $C_6H_5{\cdot}CH{:}N{\cdot}C_6H_5$. Suivant les indications fournies par l'ouvrage écrit par Vanino,[27] ce corps se recristallise dans l'alcool et donne un cristal jaunâtre qui a son point de fusion entre 53 et 54°C.

Spectres d'absorption. (1) *Azobenzène*, (2) *Phénylazométhane*, et *Azométhane*. Il semblerait que, dans les spectres d'absorption de ces trois composés (fig. 1) l'absorption des rayons lumineux par le radical azoïque –N=N– dépende grandement de la double liaison conjuguée qu'il a avec le noyau benzénique. C'est pourquoi, en substituant le radical alcoylé à un radical d'aryle, soit R–N=N–R, Ar–N=N–R et Ar–N=N–Ar (Ar: un aryle, R: un alcoyle) les bandes d'absorption varient régulièrement trahissant des influences bathochromiques et hyperchromiques. La fréquence indiquée par la centre de la bande d'absorption se porte vers une longueur d'onde plus élevée, en substituant un méthyle à un phényle (à peu près une différence de 300 dans la fréquence par chaque substitution).



1. C_6H_5-N·N-C_6H_5 (1)
2. C_6H_5-N·N-CH_3 (2)
3. CH_3-N·N-CH_3

Fig. 1.

Quant au spectre d'absorption donné par l'azométhane, nous avons pris la courbe (ligne pointillée dans la figure 1) indiquée par Hantzsch et Lifschitz,[28] pour faire une comparaison avec deux autres corps: azobenzène et phénylazométhane.

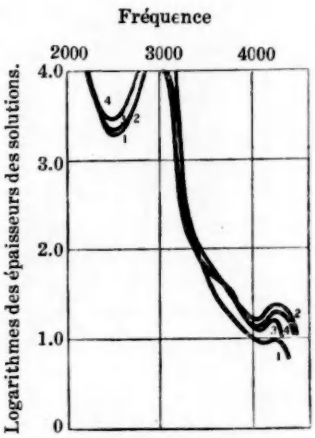
(2) *Phénylazométhane*, (3) *Phénylazoéthane*, (4) *Phénylazopropane*, et (5) *Phénylazobutane*. La figure 2 rend compte de la comparaison entre les spectres d'absorption obtenus par les quatre composés azoïques mixtes en prolongeant l'union chaînée contenue

(27) L. Vanino, "Präparative Chemie", II (1923), 468.
(28) A. Hantzsch et J. Lifschitz, *Ber.*, **45** (1912), 3011.

dans les corps étudiés. Nous avons ajouté deux nouveaux corps, le phénylazopropane et le phénylazobutane, qu'on n'a pas trouvés dans les comptes rendus de chimie.

La position du centre des spectres d'absorption est presque la même dans les quatre composés indiqués, et cela nous montre que la longueur du radical alcoylé est presque indépendante de l'absorption lumineuse et que le radical azoïque uni par le noyau benzénique $\left(\langle\bigcirc\rangle\text{-N=N-}\right)$ représente la cause principale de l'absorption lumineuse.

Baly et Tuck[29] ont les premiers exposé le résultat des spectres d'absorption du phénylazométhane, mais leurs résultats ne sont pas d'accord avec les nôtres. Puis, Hantzsch et Lifchitz,[30] Stobbe et Nowak[31] ont observé l'absorption du phénylazométhane, et ils ont admis que le phénylazométhane est obtenu d'après la méthode indiquée par Baly et Tuck, et que leur phénylazoéthane a les mêmes spectres d'absorption. Le phénylazométhane préparé par le moyen indiqué par Tafel[7] présente aussi les mêmes courbes d'absorption que le phénylazoéthane. D'après ces résultats, nous constatons que l'échantillon préparé par Baly et Tuck n'était pas pur. Quant à la bande d'absorption, nos résultats présentent un caractère plus hyperchromique que ceux obtenus par Stobbe et Nowak. Le corps utilisé par nous est, semble-t-il, plus pur et son point d'ébullition plus stabilisé.



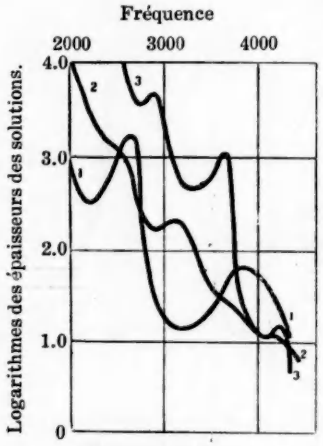
1. C_6H_5-N·N-CH_3 (2)
2. C_6H_5-N·N-CH_2-CH_3 (3)
3. C_6H_5-N·N-CH_2-CH_2-CH_3 (4)
4. C_6H_5-N·N-CH_2-CH_2-CH_2-CH_3 (5)

Fig. 2.

(1) *Azobenzène*, (6) *Phénylazophénylméthane*, et (7) *ω-Azotoluène*. Les deux composés dans lesquels l'hydrogène contenu dans le méthyle des deux corps déjà montrés dans la figure 1 est remplacé par les radicaux du phényle, ont été préparés pour être comparés avec l'azobenzène. La figure 3 représente donc la comparaison de l'azobenzène avec ces deux corps qui n'ont pas de liaison conjuguée entre le noyau benzénique et le radical azoïque. En comparant la figure 3 avec la figure 1, on note que les

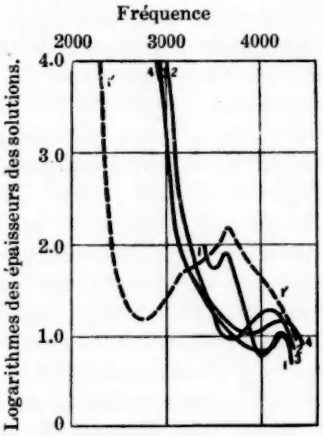
(29) E. C. C. Baly et W. B. Tuck, *J. Chem. Soc.*, **89** (1906), 982.
(30) A. Hantzsch et J. Lifschitz, *Ber.*, **45** (1912), 3011.
(31) H. Stobbe et R. Nowak, *Ber.*, **46** (1913), 2887; **47** (1914), 578.

deux corps de la figure 3 contiennent le radical azoïque qui est plutôt facile à transformer en type "*hydrazone*" plus stable qu'en type azoïque; ils ne montrent pas nettement l'absorption du radical azoïque, mais ils sont plus hypsochromiques et hypochromiques que l'azobenzène. Ceci nous explique l'influence plus ou moins grande que produit la rupture des liaisons conjuguées entre le radical azoïque et le noyau benzénique. La différence qui existe entre les colorations présentées par ces trois corps, cristal jaune-orange dans l'azobenzène, jaune et huileux dans le phénylazophénylméthane, cristal incolore dans l'ω-azotoluène, est d'accord avec la



1. C_6H_5-N=N-C_6H_5 (1)
2. C_6H_5-N=N-CH_2-C_6H_5 (6)
3. C_6H_5-CH_2-N=N-CH_2-C_6H_5 (7)

Fig. 3.



1. C_6H_5-NH-N=CH_2 (8)
1′. ,, (Baly et Tuck)
2. C_6H_5-NH-N=CH-CH_3 (9)
3. C_6H_5-NH-N=CH-CH_2-CH_3 (10)
4. C_6H_5-NH-N=CH-CH_2-CH_2-CH_3 (11)

Fig. 4.

variation de la courbe d'absorption comme le montre la figure 3. La série de trois composés déjà indiqués dans la figure 1 n'est pas suffisante pour expliquer la liaison conjuguée. Les variations de la courbe d'absorption présentées par la figure 1 risqueraient d'être attribuées aux différences qui existent entre le méthyle et le phényle. L'aparition d'une influence hypsochromique que l'on remarque dans la figure 3 pourra, cependant, en définitive provenir des relations conjuguées de liaison double, union directe du phényle avec le radical azoïque.

(8) *Formaldéhydephénylhydrazone*, (9) *Acétaldéhydephénylhydrazone*, (10) *Propylaldéhydephénylhydrazone*, et (11) *Butylaldéhydephénylhydrazone*. La figure 4 présente des courbes d'absorption du type

"hydrazone" des corps montrés dans la figure 2. Il existe déjà un certain nombre de publications concernant le spectre d'absorption observé dans l'isomérie, *"azo"* et *"hydrazone"*, mais le présent mémoire représente un spectre mesuré dans des conditions identiques, et il nous amène à admettre la différence nette qui existe entre le type *"azo"* et le type *"hydrazone"* contenus dans les composés azoïques mixtes.

Les trois courbes 2,3 et 4 données dans la figure 4 approximativement d'accord entre elles. La position du centre de leur bande d'absorption se trouve entre 3700 et 4000 de la fréquence. Tous ces corps qui contiennent le radical –N=CH– ne présentent pas d'absorption sélective dans une région visible comme l'on peut l'observer dans la figure 6. La cause en est probablement dans ce fait que le chromophore faible –N=CH– n'est pas directement joint au noyau benzénique.

Comme nous l'avons déjà dit, notre formaldéhydephénylhydrazone préparée d'après la méthode donnée par Walker a son point de fusion à 155°C., ce que Richter et Anschütz n'ont pas admis dans leur ouvrage[32] où ils ont indiqué un polymère $(C_6H_5N_2)_2(CH_2)_3$ (triméthylènephénylhydrazine) dont le point de fusion est à 183°C. Nous avons pu, par cette mesure, contrôler les dires de Richter et Anschütz qui soutenaient la non-existence de la formaldéhydephénylhydrazone et nous avons pu comprendre la différence remarquable qui existe la courbe 1 et les autres, dans la figure 4. La courbe d'absorption 1 donnée par Baly et Tuck[29] a été étudiée par ceux-ci comme la résultante d'un mélange d'un polymère ci-dessus indiqué avec un autre corps. Nous concevons des doutes sur la différence qui existe entre les courbes 1 et 1′ et l'accord global, entre la courbe 1′ et celle que présente la benzaldéhydephénylhydrazone dans la figure 6.

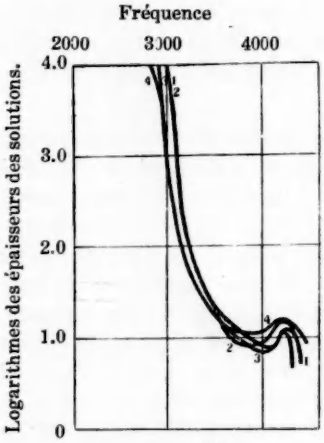
Notre courbe d'acétaldéhydephénylhydrazone est à peu près d'accord avec celles qu'ont données par Baly et Tuck,[29] Stobbe et Nowak[31] et Stevens et Ward;[33] d'autre part notre courbe d'absorption observée par la propylaldéhydephénylhydrazone n'est pas très différente de celle qui est représentée dans le mémoire de Baly et Tuck.[29]

On peut, dans les figures 2 et 4, admettre semble-t-il la différence observée dans les spectres d'absorption des deux types *"azo"* et *"hydrazone"*. Nous l'étudierons plus minutieusement et nous la discuterons dans d'autres circonstances.

(32) Richter-Anschütz, "Chemie d. Kohlenstoffverbindungen", I (12e édit., 1928), 276.

(33) H. R. Stevens et F. W. Ward, *J. Chem. Soc.*, **125** (1924), 1328.

(10) *Propylaldéhydephénylhydrazone,* (11) *Butylaldéhydephénylhydrazone,* (12) *Propanonephénylhydrazone,* et (13) *Butanonephénylhydrazone.* La figure 5 nous montre la comparaison entre la phénylhydrazone jointe au radical alcoylé sans chaîne normale et celle qui est unie par l'alcoyle contenu une chaîne normale et qui a le même nombre d'atomes de carbone. Tous les quatre corps représentés dans la figure 5 sont du type "*hydrazone*" et se ressemblent à peu près d'après les formes de leurs courbes d'absorption. La petite différence observée dans la fréquence du centre de la bande d'absorption décèle des radicaux isopropyle et isobutyle, c'est-à-dire cétonehydrazones. Ceux-ci, à la fin de l'absorption, ont des longueurs d'onde plus courtes que celles présentées par les aldéhydephénylhydrazones.



1. C_6H_5-NH-N=C$<^{CH_3}_{CH_3}$ (12)
2. C_6H_5-NH-N=C$<^{CH_3}_{CH_2\text{-}CH_3}$ (13)
3. C_6H_5-NH-N=CH-CH_2-CH_3 (10)
4. C_6H_5-NH-N=CH-CH_2-CH_2-CH_3 (11)

Fig. 5.

Baly et Tuck[29] ont déjà déterminé la courbe de la propanonephénylhydrazone laquelle est presque semblable à la nôtre.

(6) *Phénylazophénylméthane,* (7) *ω-Azotoluène,* (14) *Benzaldéhydephénylhydrazone,* et (15) *Benzalbenzylhydrazone.* Nous avons pris la benzaldéhydephénylhydrazone et la benzalbenzylhydrazone qui correspondent respectivement aux isomères déjà étudiés, phénylazophénylméthane et ω-azotoluène, pour comparer les courbes de deux types "*azo*" et "*hydrazone*".

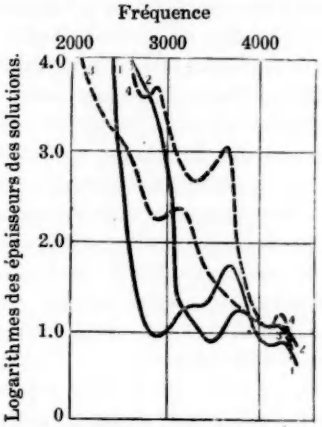
En comparant deux par deux les courbes 1 et 3, 2 et 4 de la figure 6, nous voyons que, dans les courbes 3 et 4, la bande d'absorption caractéristique donnée par "*azo*" se rapproche du type "*hydrazone*" auquel on a ajouté du phényle, en tenant compte de la courbe présentée par le phénylazométhane et l'azométhane, dans la figure 1. Ces deux courbes 3 et 4 peuvent être considérées comme celles qui sont données par le mélange des deux type "*azo*" et "*hydrazone*".

La courbe donnée par la benzaldéhydephénylhydrazone peut se retrouver dans les mémoires déjà publiés par Baly et Tuck,[29] ou par Stobbe et Nowak[34] où elle n'est guère différente de la nôtre. Stevens et Ward[33] l'ont quantitativement étudiée.

(34) H. Stobbe et R. Nowak, *Ber.,* **46** (1913), 2888.

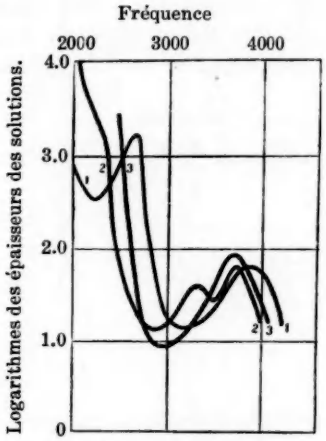
(1) *Azobenzène*, (16) *Diazoaminobenzène*, et (17) *Diméthyldiphényltétrazone*. Ley a fait remarquer les variations de couleur; orange, jaune et incolore, présentée par les trois composés, azobenzène, diaminobenzène et diphényltétrazone. A propos de cette série de corps, il a écrit, dans le "Handbuch d. Physik",[35] sur la diminution graduelle du pouvoir absorbant que présente le chromophore azoïque, quand il combine avec un radical azoté comme NH.

Puisque la diphényltétrazone, troisième composé, prise par Ley n'est pas encore connue, nous avons préparé la diméthyldiphényltétrazone,



1. C_6H_5-NH-N·CH-C_6H_5 (14)
2. C_6H_5-CH_2-NH-N·CH-C_6H_5 (15)
3. C_6H_5-N·N-CH_2-C_6H_5 (6)
4. C_6H_5-CH_2-N·N-CH_2-C_6H_5 (7)

Fig. 6.



1. C_6H_5-N·N-C_6H_5 (1)
2. C_6H_5-N·N-NH-C_6H_5 (16)
3. C_6H_5-N(CH_3)-N·N-N(CH_3)-C_6H_5 (17)

Fig. 7.

cristal incolore, d'après les indications données par Fischer,[23] pour comparer son spectre d'absorption avec celui de l'azobenzène et du diazoaminobenzène.

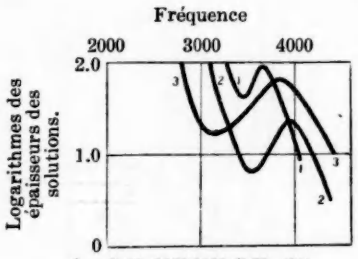
Comme nous pouvons l'observer dans la figure 7, à la fin de l'absorption, la région visible se transforme graduellement en une longueur d'onde plus petite en s'éloignant de la liaison conjuguée du radical azoïque avec le noyau benzénique. Cette variation des courbes, dans la figure 7, est en accord avec les changements que subissent les couleurs des corps ci-dessus nommés. Le centre d'absorption sélective ultra-violette donnée par le diazoaminobenzène et la diméthyldiphényltétrazone présente un carac-

(35) "Handbuch der Physik", XXI, "Licht u. Materie", (1929), 128.

tère plus bathochromique que l'azobenzène et cela nous semble se baser sur l'absorption du radical NH lui-même.

Nous notons, dans la figure 7, le pouvoir absorbant remarquable montré par la liaison conjuguée du radical azoïque avec le noyau benzénique, mais nous le voyons plus facilement, dans la figure 3, sans l'insertion du radical NH qui a une absorption ultra-violette. Notre étude actuelle a plutôt donné une explication spectrochimique de l'opinion émise par Ley et a rendu plus évidente la conclusion concernant la comparaison des courbes d'absorption que représente la figure 3.

(1) *Azobenzène,* (18) *Hydrazobenzène,* et (19) *Diphénylamine.* Pour préciser l'absorption de la phénylhydrazone en considérant l'influence exercée par le radical NH, nous avons ajouté le hydrazobenzène et la diphénylamine à l'azobenzène pour les comparer dans la figure 8.



1. C_6H_5-NH-NH-C_6H_5 (18)
2. C_6H_5-NH-C_6H_5 (19)
3. C_6H_5-N=N-C_6H_5 (1)

Fig. 8.

Le centre de bande d'absorption, dans une fréquence de 3500, est clairement observé par la diphénylamine et le hydrazobenzène, qui ne diffère par sa position avec le centre de la bande, est sensiblement hypochromique. Purvis et McCleland[36] ont déjà étudié le spectre d'absorption du hydrazobenzène, et ils n'y ont pas cependant trouvé de différence nette et rationelle concernant l'absorption que présente l'azobenzène. C'est à ce même résultat que nous sommes nous-mêmes arrivés. Ils ont probablement observé le spectre d'absorption du hydrazobenzène qui s'est déjà, en grande partie, transformé en azobenzène. Quant aux spectres d'absorption de la diphénylamine, nous en avons déjà plusieurs, et les observations de Baker[37] ne diffèrent guère des nôtres, mais elles sont un peu différentes de celles qui ont été faites par Purvis et McCleland[36] ou Lifschitz.[38]

(20) *Benzalazine,* et (21) *Benzalaniline.* Nous avons pris les deux corps préparés ci-dessus nommés pour étudier l'influence exercée par le radical –CH=N– sur l'absorption de la phénylhydrazone.

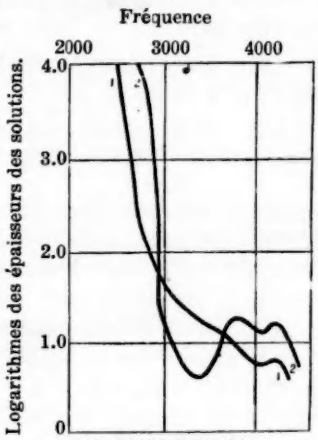
La benzalaniline jaunâtre et la benzalazine jaune ne donnent pas d'absorption sélective dans une région visible comme nous l'observons dans

(36) J. E. Purvis et N. P. McCleland, *J. Chem. Soc.,* **101** (1912), 1514.
(37) F. Baker, *J. Chem. Soc.,* **91** (1907), 1490.
(38) J. Lifschitz, *Rec. trav. chim.,* **43** (1924), 403.

la figure 9. Dans la benzalazine, le centre de bande d'absorption apparaît vers 3400 de fréquence, ce qui vient de ce que sa bande est basée sur -CH=N-. Le chromophore -CH=N- ne présente qu'un pouvoir absorbant fort hypsochromique quand il se trouve tout seul, et c'est la liaison conjuguée par rapport au noyau benzénique qui doit être considérée comme le cas du radical azoïque.

Dans le cas de la phénylhydrazone (fig. 6), puisque le noyau benzénique s'unit indirectement, en laissant un intervalle entre le radical -NH-, et le radical -CH=N-, son pouvoir absorbant est supposé plus petit que les deux composés indiqués dans la figure 9.

Baly, Tuck et Marsden[39] ont déjà publié le spectre d'absorption de la benzalaniline qui est un peu différent du résultat que nous avons obtenu.



1. C_6H_5-CH·N-C_6H_5 (21)
2. C_6H_5-CH·N-N·CH-C_6H_5 (20)

Fig. 9.

Résumé.

(1) Lorsque le radical azoïque se présente comme un chromophore bien fort, il se forme une double liaison conjuguée avec le noyau benzénique, et cette relation présente, dans ce cas, deux bandes d'absorption remarquables qui sont surtout nettement observées par la solution d'azobenzène (voir fig. 1, 2, 3 et 7).

(2) La position du centre de deux bandes d'absorption produites par les composés azoïques mixtes est indépendante de la longueur de l'alcoyle. Il nous semble que cette conclusion peut aussi confirmer le paragraphe (1) de ce résumé (voir fig. 2).

(3) Nous observons que le type *"azo"* donne naissance à deux bandes d'absorption tandis que le type *"hydrazone"* n'en montre qu'une seule (comparer fig. 2 et 4).

(4) Le spectre d'absorption observé dans le type *"hydrazone"* des corps azoïques mixtes est presque indépendant de la forme de l'alcoyle (chaîne normale ou chaîne latérale) (voir fig. 5).

(39) E. C. C. Baly, W. B. Tuck et E. G. Marsden, *J. Chem. Soc.*, **97** (1910), 590.

(5) Le pouvoir absorbant du radical azoïques dans les composés azoïques mixtes s'affaiblit par l'introduction du phényle à l'alcoyle contenu. Ce radical azoïque se change partiellement en type "*hydrazone*" plus stable (voir fig. 6).

(6) Nous avons étudié l'influence spectrochimique du radical –NH– (voir fig. 7 et 8).

(7) Nous avons examiné le pouvoir absorbant montré par le chromophore –CH=N– (voir fig. 9).

En terminant cette publication, nous avons à exprimer nos sincères remerciements à la Société "Hattori Hôkôkaï" qui a bien voulu se charger d'une partie des frais de nos expériences.

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A NEW GENERAL METHOD FOR THE SYNTHESIS OF THE DERIVATIVES OF FLAVONOL.*

By **Taichiro OYAMADA.**

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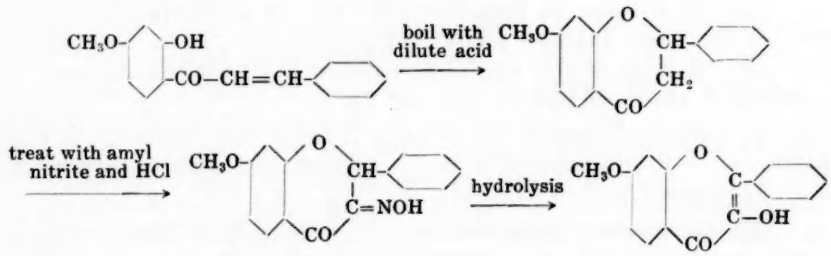
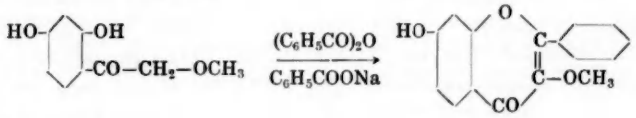
The derivatives of flavonol were first synthesised by Kostanecki and Lampe[1] from the derivatives of *o*-hydroxychalkone through isonitrosoflavanones, as shown in the following scheme:



* Translation from the original, *J. Chem. Soc. Japan*, **55** (1934), 1256.

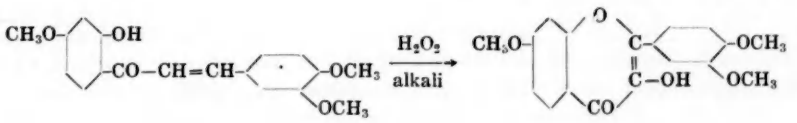
(1) *Ber.*, **37** (1904), 773.

About ten years ago, Robinson and Allan[2] suggested a new general method for their preparation:



By means of these methods a large number of the derivatives of flavonol have hitherto been synthesised.

The present author has observed that the derivatives of *o*-hydroxychalkone show an extreme facility in forming derivatives of flavonol by the action of hydrogen peroxide in the presence of alkali. A methyl alcoholic solution of 4,3′,4′-trimethoxy-2-hydroxychalkone containing hydrogen peroxide and alkali was kept at 0–5° for 12 hours, and, on acidifying, a pale yellow substance separated out. This substance, melting at 185°, was proved to be identical with 7,3′,4′-trimethoxy-3-hydroxyflavone by the mixed melting point. The yield amounted to about 80%.

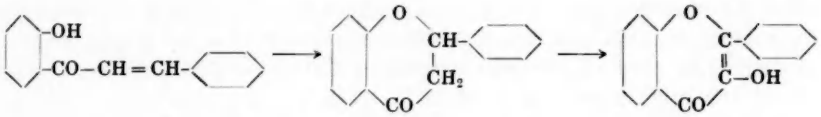


The similar reactions were carried out with 2-hydroxychalkone, 2-hydroxy-4′-methoxychalkone, and 2-hydroxy-3′,4′-dimethoxychalkone, and the corresponding derivatives of flavonol were obtained in good yields. It can naturally be considered that this method is generally applicable for synthesis of the derivatives of flavonol. Owing to the simplicity of the procedure and to the excellent yield, it may be said to be a new convenient method for preparation.

Weitz and Scheffer[3] first studied the action of hydrogen peroxide on chalkone in the aqueous-alcoholic solution and obtained benzalacetophenone-oxide from benzalacetophenone. Recently, Baker and Robinson[4] applied this reaction to 2-acetoxy-4-methoxychalkone, but without success, and reported that the reaction resulted merely in the hydrolysis of the acetoxy-group. But the present author has observed that the above-mentioned derivatives of *o*-hydroxychalkone easily give the correspond-

(2) *J. Chem. Soc.*, **125** (1924), 2192.
(3) *Ber.*, **54** (1921), 2344.
(4) *J. Chem. Soc.*, **1932**, 1798.

ing flavonols under the conditions described above. Now it is interesting to consider the mechanism of the formation of flavonol from *o*-hydroxychalkone. We first suppose that the formation of the oxide as an intermediate product may take place, but it is difficult to explain how the oxide is converted into flavonol. On the other hand, we can also consider that *o*-hydroxychalkone isomerises to flavanone which may be oxidised to flavonol under these conditions. The latter view was supported by the experimental fact that *o*-hydroxychalkone easily gives flavanone with alkali alone and the resulting flavanone is subsequently converted into flavonol in an excellent yield by the action of hydrogen peroxide in the presence of alkali. Hence, the mechanism of the formation of flavonol is accounted for by the following scheme:



That of the formation of the other three derivatives of flavonol will also be explained as in the above case.

By the action of hydrogen peroxide in the presence of alkali, 4′-methoxyflavanone and 7,3′,4′-trimethoxyflavanone were oxidised to 4′-methoxyflavonol and 7,3′,4′-trimethoxyflavonol respectively in good yields. It is of interest to note that a derivative of flavanone is directly converted into a derivative of flavonol by such a simple oxidation. In the early stage of the investigation of the derivatives of flavonol, attempts to obtain flavonol from flavone by oxidation were made by Kostanecki and his collaborators,[5] but without success. The present author has succeeded in preparing it from flavanone by oxidation.

Experimental.

Preparation of 7, 3′, 4′-Trimethoxy-3-hydroxyflavone from 4, 3′, 4′-Trimethoxy-2-hydroxychalkone. To a solution of 4,3′,4′-trimethoxy-2-hydroxychalkone (1.5 g.) in methyl alcohol (30 c.c.), 15% aqueous hydrogen peroxide (4 c.c.) and 16% aqueous sodium hydroxide (10 c.c.) were added under cooling. After being allowed to stand at 0–5° for 12 hours, the solution was acidified with dilute sulphuric acid and diluted with water. The precipitate was recrystallised from alcohol, pale yellow needles melting at 185°, and showing no depression of melting point by admixture with 7,3′,4′-trimethoxy-3-hydroxyflavone synthesized by the Kostanecki method. The yield was 1.2 g. (Found: C, 65.62; H, 5.05. Calc. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.87%.)

(5) *Ber.*, **35** (1902), 1679.

Preparation of 3-Hydroxyflavone (Flavonol) from *o*-Hydroxychalkone. *o*-Hydroxychalkone (1 g.) was dissolved in methyl alcohol (20 c.c.), and 15% aqueous hydrogen peroxide (3 c.c.) and 16% aqueous sodium hydroxide (5 c.c.) were added. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water, when a colourless substance separated out. It was recrystallised from alcohol, needles melting at 169–170°. This melting point coincides with that of flavonol.[6] The yield was 0.8 g. (Found: C, 75.35; H, 4.58. Calc. for $C_{15}H_{10}O_3$: C, 75.63; H, 4.20%.)

3-Methoxyflavone (Methylflavonol). 3-Hydroxyflavone (0.5 g.) was methylated with diazomethane in ethereal solution. On recrystallising from alcohol, colourless needles, m.p. 114°, were obtained. The yield was 0.5 g. 3-Methoxyflavone which prepared by Hattori[7] melts at 107°. (Found: C, 75.97; H, 4.98. Calc. for $C_{16}H_{12}O_3$: C, 76.19; H, 4.76%.)

3-Acetoxyflavone. 3-Hydroxyflavone (0.5 g.) was acetylated with acetic anhydride and fused sodium acetate. The product forms colourless crystals melting at 110–111°. Kostanecki and Szabranski[8] gave 110-111° as its melting point. Yield, 0.2 g. (Found: C, 73.00; H, 4.56. Calc. for $C_{17}H_{12}O_4$: C, 73.21; H, 4.29%.)

Preparation of 4′-Methoxy-3-hydroxyflavone from 4′-Methoxy-2-hydroxychalkone. To a solution of 4′-methoxy-2-hydroxychalkone (1 g.) in methyl alcohol (35 c.c.), 15% aqueous hydrogen peroxide (2 c.c.) and 16% aqueous sodium hydroxide (2 c.c.) were added under cooling. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water. The pale yellow crystals which separated were collected and recrystallised from alcohol, pale yellow needles, m.p. 230–232°. Edelstein and Kostanecki[9] gave 231–232° as the melting point. Yield, 0.7 g. (Found: C, 71.57; H, 4.70. Calc. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.48%.)

3, 4-Dimethoxyflavone. 4′-Methoxy-3-hydroxyflavone (0.5 g.) was methylated with diazomethane in ethereal solution. The raw product was recrystallised from alcohol, when it melted at 90–92°. The yield was 0.3 g. (Found: C, 72.15; H, 5.21. Calc. for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96%.)

Preparation of 3′, 4-Dimethoxy-3-hydroxyflavone from 3′, 4′-Dimethoxy-2-hydroxychalkone. 3′,4′-Dimethoxy-2-hydroxychalkone (1.3 g.) was dissolved in methyl alcohol (15 c.c.), and 15% aqueous hydrogen peroxide (2 c.c.) and 16% aqueous sodium hydroxide (3 c.c.) were added under cooling. After standing overnight in the ice-chest, the alkaline solution was acidified with dilute sulphuric acid and diluted with water, when a yellow substance separated out. On recrystallising from alcohol, pale yellow crystals m.p. 200–202° were obtained. Hattori[10] gave 202° as its melting point. Yield, 1 g. (Found: C, 68.66; H, 4.84. Calc. for $C_{17}H_{14}O_5$: C, 68.79; H, 4.69%.)

3,3′, 4′-Trimethoxyflavone. 3′,4′-Dimethoxy-3-hydroxyflavone (0.5 g.) was methylated with diazomethane in ethereal solution and the product was then purified, when

(6) *Ber.*, **37** (1904), 2820.
(7) *Acta Phytochimica*, **4** (1928), 44.
(8) *Ber.*, **37** (1904), 2820.
(9) *Ber.*, **38** (1905), 1507.
(10) This Bulletin, **2** (1927), 175.

almost colourless crystals, m.p. 168–169°, were obtained. Hattori[10] gave 168–169° as its melting point. The yield was 0.2 g. (Found: C, 69.04; H, 5.36. Calc. for $C_{18}H_{16}O_5$: C, 69.23; H, 5.12%.)

Preparation of Flavanone from o-Hydroxychalkone. To a solution of *o*-hydroxychalkone (1 g.) in methyl alcohol (15 c.c.), 16% aqueous sodium hydroxide (4 c.c.) was added. After standing overnight in the ice-chest, the solution was diluted with water, when a colourless substance separated out. On recrystallising from dilute alcohol, colourless prisms, m.p. 75–76°, were obtained. No alternation of melting point was observed on mixing it with flavanone obtained by the usual method. Yield, 0.8 g.

Preparation of 3-Hydroxyflavone (Flavonol) from Flavanone. Flavanone (0.3 g.) in methyl alcohol (15 c.c.) was mixed with 15% aqueous hydrogen peroxide (2 c.c.) and 16% sodium hydroxide (3 c.c.) under cooling. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water. The colourless crystals which separated were recrystallised from alcohol, colourless needles, m.p. 169–170°. No alternation of melting point was observed on mixing it with flavonol obtained by the method described on page 185. Yield, 0.25 g.

Preparation of 4′-Methoxy-3-hydroxyflavone from 4′-Methoxyflavanone. 4′-Methoxyflavanone (0.5 g.) was dissolved in methyl alcohol (10 c.c.), and 15% aqueous hydrogen peroxide (2 c.c.) and 16% aqueous sodium hydroxide (2 c.c.) were added under cooling. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water, when a pale yellow substance separated out. It was recrystallised from alcohol, pale yellow needles, m.p. 232°. It proved to be identical with 4′-methoxy-3-hydroxyflavone by the mixed melting point. Yield, 0.4 g.

Preparation of 7, 3′, 4′-Trimethoxy-3-hydroxyflavone from 7, 3′, 4′-Trimethoxyflavanone. 7,3′,4′-Trimethoxy-3-hydroxyflavone was directly prepared from 7,3′,4′-trimethoxyflavanone similarly as described above.

In conclusion, the author wishes to express his sincere thanks to Professor Kinzo Kafuku for his kind guidance and encouragement.

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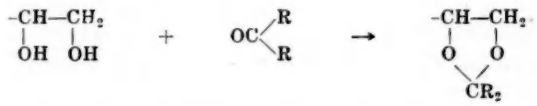
ACETONE-COMPOUNDS OF SOME *α*-HYDROXY-ACIDS AND THEIR RAMAN SPECTRA.*

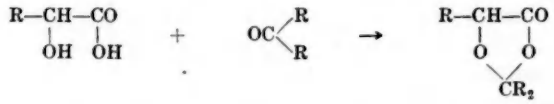
By Haruomi ÔEDA.

Received February 22nd, 1935. Published May 28th, 1935.

Polyhydric compounds, which contain two hydroxyls in *α*-positions, condense with a carbonyl compound producing cyclic acetals in the presence of dehydrating agents.



It is known that some *α*-hydroxy-acids behave similarly towards carbonyl and form compounds having a heterocyclic ring of the same type.



The preparation of such derivatives of *α*-hydroxy-acids was reported by Wallach,[1] Leipen,[2] van Ekenstein,[3] and several other investigators. Formaldehyde, benzaldehyde, and acetone can be mentioned as the reactants on *α*-hydroxy-acids. Restricting to the acetone compounds, following works are cited from the literature.

In 1923 Willstätter[4] prepared acetone compounds of glycollic acid (b.p. 41° under 11 mm.), mandelic acid (m.p. 47.5–48°), and benzilic acid (m.p. 48°). In 1927 those of tartaric acids (*l* and *d*, m.p. 102°; *r*, 88.5°; *i*, 96–97°) and of quinic acid (m.p. 141°) were synthesized by H. O. L. Fischer.[5] As the dehydrating agent, Willstätter used concentrated sulphuric acid or anhydrous copper sulphate, while zinc chloride and

* Studies on Hydroxy-acids and their Derivatives. II.

(1) O. Wallach, Th. Heymer, *Ber.*, **9** (1876), 545.

(2) R. Leipen, *Monatsh.*, **9** (1888), 45.

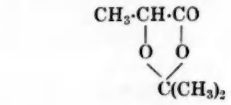
(3) W. A. Ekenstein, C. A. Lobry de Bruyn, *Rec. trav. chim.*, **18** (1899), 305; **20** (1901), 331; **21** (1902), 310.

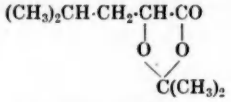
(4) R. Willstätter, Fr. Königsberger, *Ber.*, **56** (1923), 2107.

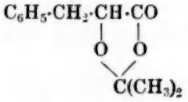
(5) H. O. L. Fischer, C. Taube, *Ber.*, **60** (1927), 485.

phosphorus pentoxide were recommended by H. O. L. Fischer and Smith[6] respectively.

The present author tried the preparation of acetone compounds of other α-hydroxy-acids and isolated the following:

Acetone-lactic acid  b.p. 49–49.5° under 11 mm.

Acetone-leucic acid  b.p. 84.5–85.5° under 13 mm.

Acetone-phenyl-lactic acid  m.p. 63–64°.

The latter two are formed by dehydration either with sulphuric acid or zinc chloride (better yield is obtained with the former), but the acetone compound of lactic acid is very sensitive to hydrolysis and can be prepared only with sulphuric acid under the special precautions that it never come in contact with water during its isolation.

Little was studied on the properties of acetone-hydroxy-acids and the only fact hitherto described is their instability towards warm dilute alkali. The author intends to carry out some investigations on the compounds of this class and the Raman spectra were first studied.

Raman Spectra. The acetone compounds of lactic acid and leucic acid were selected as materials. At room temperature, they are liquid, which provides every facility for the study of Raman spectra.

On the Raman spectra of compounds having five-membered saturated ring, informations are few except cyclopentane and its derivatives[7] and some of the anhydrides of dibasic acids.[8] From the Raman spectra of two above-mentioned compounds photographed by the author, the following conclusion can be derived.

(a) C·H-Frequencies. In both of the spectra, the frequencies close up and over 2900 cm.$^{-1}$ (2869, 2940, 2993 in acetone-lactic acid (I) and

(6) L. Smith, J. Lindberg, *Ber.*, **64** (1931), 505.

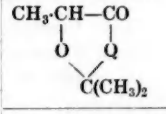
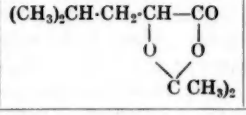
(7) Weiler, *Z. Physik*, **69** (1931), 586; Canal, *Compt. rend.*, **194** (1932), 1574. L. Piaux, *Compt. rend.*, **197** (1933), 1647; **198** (1934), 1496.

2868, 2902, 2939, 2994 in acetone-leucic acid (II)) are lines usually assigned as "C·H-valency-frequencies". No C·H-frequency which exceeds 3000 cm.$^{-1}$ is found in the spectra. The frequencies 1448 cm.$^{-1}$ in I and 1446 cm.$^{-1}$ in II are assigned as "C·H-deformation-frequencies".

(b) C:O-Frequency. The present compounds contain a carbonyl group in the molecules. The frequencies 1790 cm.$^{-1}$ in I and 1787 cm.$^{-1}$ in II can be attributed to this group, although the values observed here seem rather high for such frequencies.

According to the detailed study of Kohlrausch,[8] the C:O-frequency is said to be sensible to the constitutive effect of adjacent groups. It shows minimum value in free acids (mean 1660 cm.$^{-1}$) and it increases in ketones, aldehydes, and esters (mean of esters 1732 cm.$^{-1}$) in the order mentioned. In acid anhydrides, which show some similarity in structure with the present compounds, the value increases furthermore; 1740–1754 cm.$^{-1}$ are observed in six kinds of anhydrides of monobasic acids and 1774–1782 cm.$^{-1}$ in four kinds of anhydrides of dibasic acids (inner anhydrides). In addition to these, it was pointed out also by Kohlrausch that the more sensitive the compound to hydrolysis, the higher is the value of C:O-frequency, Table 1.

Table 1.

Phthalide	$C_7H_4<\begin{matrix}CO\\CH_2\end{matrix}>O$	1753
Phthalic anhydride	$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O$	1775
Benzoic anhydride	$C_6H_5\cdot CO\cdot O\cdot OC\cdot C_6H_5$	1776
Benzoyl peroxide	$C_6H_5\cdot CO\cdot O\cdot O\cdot OC\cdot C_6H_5$	1781
Acetone-lactic acid		1790
Acetone-leucic acid		1787

The present compounds have the similar cyclic structure as anhydrides of dibasic acids and show marked sensitivity to hydrolysis and it is easily understood from the study of Kohlrausch that the C:O-frequencies in these compounds show the values as high as 1787–1790 cm.$^{-1}$.

(c) Other frequencies. Among other frequencies, the two adjacent ones, 623, 706 cm.$^{-1}$ in I and 623, 700 cm.$^{-1}$ in II are sharp and strong and are very conspicuous in each of two spectra.

(8) K. Kohlrausch, A. Pongratz, R. Seka, *Ber.*, **66** (1933), 1.

Experimental Part.

Preparation of acetone-compounds of α-hydroxy-acids.

Acetone-lactic acid. Lactic acid (Takeda; 100 g.) was dissolved in dry acetone (400 c.c.). The solution was kept at -5--10° and concentrated sulphuric acid (300 g.) was added with mechanical stirring in the course of two hours. Benzene was poured repeatedly (total volume, 1000 c.c.) to the above solution and the product was thoroughly extracted.

To the combined benzene solution freshly ignited sodium sulphate was added and dry ammonia was passed to neutralize the remaining acid. After standing overnight, the benzene was removed under reduced pressure and the residual oil was subjected to vacuum distillation, when the main part distilled at 57–58° under 18 mm. and it amounted to 43.2 g., corresponding to 30 mol% assuming that the lactic acid was pure. After refractionation, the part distilling at 49–49.5° under 11 mm. was taken for analysis. The acetone-compound is readily hydrolyzed with warm dilute alkali and the components can be determined as follows: The weighed sample was completely hydrolyzed with an excess of N/10-alkali by warming on water bath. After cooling, the remaining alkali was titrated with N/10-acid. (Found: Saponification equivalent, 130.6. Calc. for $C_6H_{10}O_3$: 130.1). The weighed sample was hydrolyzed with an excess of N-alkali in a tightly stoppered bottle. After cooling, acetone was determined by Messinger's method as usual. (Found: acetone, 44.07. Calc. for $C_6H_{10}O_3$: 44.65%.)

Acetone-leucic acid. (a) *By sulphuric acid method.* Leucic acid (40 g., 0.30 mol) (m.p. 73°, prepared from natural leucine) was dissolved in acetone (110 c.c.) and the solution was cooled at -10--20°. Concentrated sulphuric acid (25 g.) was gradually added with constant stirring. After 30 minutes, the reaction product was poured into an excess of ice-cooled 10% sodium carbonate solution to remove acid, whereupon an oil gradually accumulated on the surface of the solution. The oily layer was separated and the carbonate solution was thoroughly extracted with ether, to which the above oil was put together. After removing ether, the residual oil was distilled in vacuum; the part distilling at 90–92.5° under 18 mm. amounted to 33.7 g., corresponding to 64 mol%. (Found: Saponification equivalent, 173.6; acetone, 33.32. Calc. for $C_9H_{16}O_3$: sap. equ., 172.1; acetone, 33.72%.)

(b) *By zinc chloride method.* Leucic acid (20 g., 0.15 mol.) was dissolved in dry acetone (50 c.c.), to which a suspension of zinc chloride (40 g.) in acetone (100 g.) was gradually added. After standing overnight, acetone was distilled off in vacuum and ether (500 c.c.) was added and the mixture was extracted with water to remove zinc chloride. After drying, ether was expelled and the residual oil was subjected to distillation. The part distilling at 91–95° under 21 mm. (3.9 g., corresponding to 15 mol%) was collected, but it was contaminated with mesityl oxide. It required repeated fractionation to remove the impurity completely.

Acetone-phenyl-lactic acid. (a) *By sulphuric acid method.* Phenyl-lactic acid (40 g., 0.24 mol) (m.p. 124°; prepared from natural phenylalanine) was put into acetone (110 c.c.) and was treated with concentrated sulphuric acid (24 g.) just in the same manner as in the case of leucic acid. The solution was poured into an excess of ice-cooled 10% sodium carbonate solution and the acetone compound separated as crystals. It amounted to 43 g. after drying overnight. Yield, 88 mol%. It melted

at 63–64° after recrystallisation from alcohol. (Found: saponification equivalent, 206.4; acetone, 27.82. Calc. for $C_{12}H_{14}O_3$: sap. eq., 206.1; acetone, 28.17%.)

(b) *By zinc chloride method.* From 15 g. of the hydroxy-acid, 50 c.c. of dry acetone, and 23 g. of zinc chloride; 5.2 g. of the acetone-compound was obtained, yield 28 mol%.

Raman Spectra.

The Raman spectra were taken in the laboratory of Prof. Mizushima by his and his collaborators' courtesy. Every appliance for Raman spectrum here used is of

Table 2. Acetone-lactic acid.

No.	Intensity	$\Delta\nu$ in cm.$^{-1}$	No. in which $\Delta\nu$ is equal
1	m.	k– 114	1–15
2	w.	k– 258(q–2941)	2–26–31
3	w.	k– 310(q–2993)	3–27–32
4	w.	k– 348(p–2996) (o–2936)	4–27–32 4–26–31
5	w.	k– 412(o–3000)	5–27–32
6	w.	k– 526	6–18
7	v.s.	k– 623	7–19
8	s.	k– 705	8–20
9	s.	k– 786	9–21
10	w.	k– 813(i– 624)	10– 7–19
11	w.	k– 883	11–22
12	w.	k– 934	12–23
13	w.	k– 984	13–24
14	m. b.	k–1449	14–28
15	s.	e– 115	15– 1
16	w.	e– 250	—
17	m.	e– 329	—
18	w.	e– 529	18– 6
19	v.s.	e– 622	19– 7
20	s.	e– 707	20– 8
21	s.	e– 784	21– 9
22	w.	e– 884	22–11
23	w.	e– 933	23–12
24	w.	e– 987	24–13
25	m.	e–1099(k–2868)	25–30
26	v.s.	e–1176(k–2943)	26–31
27	v.s.	e–1227(k–2994)	27–32
28	s. b.	e–1447	28–14
29	m.	e–1790	—
30	m.	e–2870	30–25
31	v.s.	e–2937	31–26
32	v.s.	e–2992	32–27

$\Delta\nu$: 115(s.), 250(w.), 329(m.), 528(w.), 623(v.s.), 706(s.), 785(s.), 884(w.), 934(w.), 986(w.), 1448(s. b.), 1790(m.), 2869(s.), 2940(v.s.), 2993(v.s.).

Table 3. Acetone-leucic acid.

No.	Intensity	$\Delta\nu$ in cm.$^{-1}$	No. in which $\Delta\nu$ is equal
1	w.	k– 223(p–2871)	1–26–32
2	m.	k– 258(q–2941)	2–28–34
3	w.	k– 278(o–2866)	3–26–32
4	m.	k– 317(q–3000)	4–29–35
5	w.	k– 352(o–2940) (p–3000)	5–28–34 5–29–35
6	w.	k– 415(o–3003)	6–29–35
7	w.	k– 518	7–19
8	v.s.	k– 623	8–20
9	s.	k– 699	9–21
10	w.	k– 808(i– 619)	10– 8–20
11	s.	k– 828	11–22
12	w.	k– 925	12–23
13	w.	k– 958	13–24
14	w.	k–1009	14–25
15	w.	k–1141(e+ 626)	15– 8–20
16	s. b.	k–1447	16–30
17	w.	e– 359	—
18	w.	e– 429	—
19	w.	e– 524	19– 7
20	v.s.	e– 622	20– 8
21	s.	e– 700	21– 9
22	s.	e– 829	22–11
23	w.	e– 928	23–12
24	m.	e– 957	24–13
25	w.	e–1001	25–14
26	s.	e–1103(k–2870)	26–32
27	s.	e–1136(k–2903)	27–33
28	v.s.	e–1172(k–2939)	28–34
29	v.s.	e–1229(k–2996)	29–35
30	s. b.	e–1444	30–16
31	m.	e–1787	—
32	s.	e–2865	32–26
33	s.	e–2901	33–27
34	v.s.	e–2939	34–28
35	v.s.	e–2992	35–29

$\Delta\nu$: 359(w.), 429(w.), 521(w.), 623(v.s.), 700(s.), 829(s.), 927(w.), 958(m.), 1005(w.), 1446(s. b.), 1787(m.), 2868(s.) 2902(s.), 2939(v.s.), 2994(v.s.).

their own construction.(9) 1. Light source: two mercury lamps, 30 cm. long (100 v.–10 amp.). 2. Spectrograph: an apparatus with large aperture (1:5) having a dispersion of 12 Å per mm. at 4000 Å. 3. The breadth of the slit: 0.1 mm. 4. Photographic plates: "Agfa Isochromplatten." 5. Time of exposure: 2.5 hours (3.5 hrs. in the case when quinine sulphate filter was used). 6. The relative intensity of Raman spectra was classified into four grades (by visual estimation), namely, very strong (v.s.), strong (s.), medium (m.) and weak (w.). 7. The Raman apectra were taken twice for each sample, once with the filter, and the mean value of the frequencies in both plates are shown in Tables 2 and 3. 8. Materials: purified by repeated fractionation in vacuum through a 6 cm. Widmer column, in each experiment, 25 c.c. of the pure sample was put into the scattering tube.

Acetone-lactic acid,	b.p. 58.0–58.5°C. under 18 mm.
Acetone-leucic acid,	b.p. 84.5–85.5°C. under 13 mm.

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author wishes to express his sincere thanks to Prof. K. Matsubara for the kind inspection of this paper. His best thanks are also due to Prof. S. Mizushima and Mr. Y. Morino for their valuable instructions in the study of Raman spectrum and to Dr. Y. Takayama for his constant encouragements during this work.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL.

II. THE CONSTITUTION OF HIRAGONIC ACID $C_{16}H_{26}O_2$.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received February 25th, 1935. Published May 28th, 1935.

In the previous paper,(1) the authors described the isolation of hiragonic acid $C_{16}H_{26}O_2$ from Japanese sardine oil. The present paper records the results of the experiments concerning the constitution of this acid.

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(9) The detailed description of the apparatus is given by Mizushima, Morino, and Higasi, *Scientific Papers of the Institute of Physical and Chemical Research, Japan*, **25** (1934), 159–221; *Physik. Z.*, **35** (1934), 905–911.

* Translated from the paper published in Japanese in the Report of Tokyo Imperial Industrial Research Laboratory, **27** (1932), No. 2.

(1) Toyama and Tsuchiya, this Bulletin, **4** (1929), 83.

For the determination of the positions of three ethylenic linkings in hiragonic acid, its methyl ester was oxidised by the permanganate method and also by the ozonide method, and the products were examined. Among the oxidation products of methyl hiragonate by the permanganate method, acetic acid $CH_3 \cdot COOH$, succinic acid $HOOC \cdot (CH_2)_2 \cdot COOH$, and methyl hydrogen adipate $HOOC \cdot (CH_2)_4 \cdot COOCH_3$ were identified. The products obtained by the ozonide method contained, besides the above-mentioned three compounds, acetaldehyde $CH_3 \cdot COH$ and semi-aldehyde of methyl hydrogen adipate $HOC \cdot (CH_2)_4 \cdot COOCH_3$, and also the presence of semi-aldehyde of succinic acid $HOC \cdot (CH_2)_2 \cdot COOH$ and succinic aldehyde $HOC \cdot (CH_2)_2 \cdot COH$ (or its polymerised products) was indicated. It is seen from these results that the free hiragonic acid has the groups: $CH_3 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_4 \cdot COOH$, of which hiragonic acid should contain two of the $=CH \cdot (CH_2)_2 \cdot CH=$ group, since it has three ethylenic linkings. This is also verified by the fact that the actual yield of the oxidation products having four carbon atoms was considerably higher than the value obtainable by assuming only one $=CH \cdot (CH_2)_2 \cdot CH=$ group. The constitution of hiragonic acid was thus established as $\Delta^{6:7,\ 10:11,\ 14:15}$-hexadecatrienoic acid which is expressed by the following formula:

$$CH_3 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_4 \cdot COOH$$

Besides hiragonic acid, two other unsaturated C_{16}-acids have hitherto been found with certainty in natural fatty oils. These are zoomaric acid, which occurs widely in marine animal oils, and lycopodium-oleic acid in lycopodium oil. In comparison of these two acids, it should be mentioned here that the positions of three ethylenic linkings in hiragonic acid differ entirely from those in zoomaric and lycopodium-oleic acids. Whilst the ethylenic linking of zoomaric acid[2] lies in 9:10-position and that of lycopodium-oleic acid[3] in 12:13-position, hiragonic acid has three ethylenic linkings in 6:7-, 10:11- and 14:15-positions, but no ethylenic linking in 9:10- or in 12:13-position.

Experimental.

1. Preparation of Methyl Hiragonate. For the preparation of methyl hiragonate used in these experiments, a methyl ester fraction containing a large amount of highly unsaturated C_{16}- and C_{18}-acids as their methyl esters was prepared first from the sardine oil, and it was then converted into bromides, from which the ether insoluble,

(2) Toyama, *J. Soc. Chem. Ind. Japan*, **30** (1927), 603.
(3) K. H. Bauer and W. Piners, *Pharm. Zentralhalle*, **71** (1930), 33.

but benzene soluble portion was separated. Debromination of this portion followed by a repeated fractionation gave a fraction corresponding to methyl hiragonate.

(i) *Preparation of methyl ester fraction in which highly unsaturated* C_{16}- *and* C_{18}-*acid are concentrated.* The Japanese sardine oil used in these experiments had d_4^{20} 0.9265, n_D^{20} 1.4795, saponification value 190.0, iodine value by the Rosenmund-Kuhnhenn method 164.0, and the mixed fatty acids yielded 54.14% of ether insoluble bromides. It was converted into ethyl esters[4] by ethanolysis, and the latter were subjected to the distillation, by which the fraction boiling below 215°/10 mm. and the fraction boiling over 215°/10 mm. were collected separately. Whilst the fraction boiling below 215°/10 mm. was used in these experiments, the higher fraction was used for the examination of highly unsaturated C_{20} and C_{22}-acids which will be reported later. Sixty kg. of the ethyl esters gave 28.5 kg. of the fraction boiling below 215°/10 mm. This was converted into free fatty acids by saponification followed by acidification in the usual way, the latter were dissolved in 5 times of their weight of 85% methanol, allowed to cool down to about 10°, and the separated crystals consisting largely of saturated fatty acids were filtered. The filtrate was neutralised with aqueous lithium hydroxide solution (2.5%), the insoluble lithium soaps formed were removed by filtration, and on acidification of the filtrate there were obtained 7.5 kg. of 85% methanol, allowed to cool down to about 10°, and the separated crystals consistjected to fractional distillation, which yielded 5.9 kg. of a fraction boiling below 215°/15 mm. It had saponif. value 199.6 and iodine value by the Rosenmund-Kuhnhenn method 182.8, and was considered to contain a large proportion of highly unsaturated C_{16}- and C_{18}- acids as their methyl esters.

(ii) *Preparation of ether insoluble bromides and separation of the bromides by means of benzene.* From the methyl ester fraction boiling below 215°/15 mm., the ether insoluble bromides were prepared in the following manner: 100 g. of the methyl ester fraction was dissolved in 1 l. of ether and cooled to –10°. Bromine, dissolved in an equal part of glacial acetic acid, was added with constant stirring until the brown colouration remained permanent. After standing for 15 hours at 2–3°, the supernatant ethereal solution was removed by decantation, the residual precipitate of insoluble bromides was washed 2 to 3 times with cold ether by decantation as before, and then transferred on the filter where it was washed thoroughly until the washings became colourless. In total, about 2 l. of ether was used for washings. The precipitate appeared to be soluble in ether to a certain extent. For the recovery of the solid bromides dissolved in the washings, the united washings were treated with sodium thiosulphate to remove the excess of bromine, concentrated by distilling off a portion of ether, and on cooling the solid bromides separated from the solution. In our previous experiment,[5] the precipitate of solid bromides to be recovered was filtered and washed with ether, but a large amount of ether was required in order to remove oily bromides which adhere tenaciously to the precipitate, and the washing of precipitate was not successful as the precipitate itself dissolved in ether before it was completely washed. In this experiment, the precipitate was filtered and it was boiled with five volumes of alcohol, then cooled down to room temperature and filtered with suction. By repeating the washing in this way with the use of alcohol four times, the filtrate became

(4) Excepting this case, the methyl esters were used instead of the ethyl esters.
(5) This Bulletin, **4** (1929), 83.

colourless and a white powder of bromide was obtained. The latter was added to the main portion of ether insoluble bromides obtained before. The ether insoluble bromides thus obtained were then treated with benzene in the following manner: 20 g. of ether insoluble bromides were refluxed with 1.5 l. of benzene for about 40 minutes, and filtered while hot. From the filtrate, the dissolved bromides were recovered by distilling off benzene. By these treatments, 5.9 kg. of the methyl ester fraction yielded 1.5 kg. of benzene soluble, but ether insoluble bromides and 900 g. of benzene insoluble bromides.

(iii) *Debromination of benzene soluble, but ether insoluble bromides and fractionation of debrominated products.* For the debromination of benzene soluble bromides, 100 g. of the bromides was mixed with 50 g. of zinc powder, and the mixture was dropped gradually into a flask containing 150 c.c. of alcohol. The flask was immersed in cold water to avoid a violent heat evolution. When no further evolution of heat occurred, the flask was placed on the water-bath, and 150 c.c. of 5N alcoholic solution of hydrogen chloride was added in the course of 1.5 hours; during the reaction further 50 g. of zinc powder was added in several portions. After all the alcoholic solution of hydrogen chloride has been added, the solution was refluxed for another 1 hour, and the filtered. The residue, which seemed to contain some unchanged bromides, was heated with 100 c.c. of alcohol and 25 g. of zinc powder on the water-bath with an addition of 50 c.c. of alcoholic solution of hydrogen chloride during 30 minutes. After heating for one hour more, the alcoholic solution was filtered. The alcoholic solutions and the washings obtained by these treatments were combined and the debrominated product which was separated by an addition of a large quantity of water was taken up with ether. Since it was suspected that the debrominated product might contain a small portion of unsaponifiable substance, it was saponified, the unsaponifiable substance was removed by extraction with ether, and the fatty acids liberated from the soap solution on acidification were reconverted into methyl esters. These were subjected to a repeated fractionation, by which a fraction boiling at 186–188°/15 mm. was finally obtained as methyl hiragonate; yield 58 g. It had the following constants: d_4^{15} 0.9155, d_4^{20} 0.9122, n_D^{15} 1.4783, n_D^{20} 1.4764, molecular refraction 81.74 (calc. for $C_{17}H_{28}O_2$: 80.96), saponif. value 212.8 (calc. 212.4), iodine value by the Rosenmund-Kuhnhenn method 288.7 (calc. 288.2). On brominating in ethereal solution, it gave an ether-insoluble bromide (yield 57%) which melted at about 180° to a light yellow liquid (Found: Br, 64.61. Calc. for $C_{17}H_{28}O_2Br_6$: Br, 64.47%).

Hiragonic acid was obtained on saponification of its methyl ester followed by acidification (Found: C, 76.69; H, 10.32. Calc. for $C_{16}H_{28}O_2$: C, 76.74; H, 10.47%). It had the following constants: d_4^{15} 0.9330, d_4^{20} 0.9296, n_D^{15} 1.4870, n_D^{20} 1.4850, molecular refraction 77.13 (calc. for $C_{16}H_{28}O_2$: 76.22), neutralisation value 223.1 (calc. 224.2), iodine value by the Rosenmund-Kuhnhenn method 303.1 (calc. 304.4). Bromination of hiragonic acid in ethereal solution gave an ether insoluble bromide (yield 57%) which melted at about 190° (Found: Br, 65.84. Calc. for $C_{16}H_{28}O_2Br_6$: Br, 65.71%). Hydrogenation of hiragonic acid yielded palmitic acid which after recrystallisation from 90% alcohol showed neutralisation value 218.5 (calc. 219.0), m.p. and mixed m.p. 62.5°. It should be noted here that hiragonic acid and its methyl ester showed a slight exaltation of molecular refraction; the cause of this exaltation is unknown to us.

2. Oxidation of Methyl Hiragonate by the Permanganate Method. Methyl hiragonate (20 g.) was dissolved in 200 g. of acetone, the solution was gently boiled.

and 200 g. of powdered potassium permanganate was added in the course of 5 hours. When all the permanganate has been added, the solution was continued to reflux for 5 hours more, and then the acetone was removed by distillation. The residue was mixed with 400 c.c. of water, and a current of sulphur dioxide was passed through the mixture until the excess of permanganate and the insoluble oxides of manganese have disappeared completely. An oily portion (**A**), which separated from the aqueous solution, was collected on a filter, and the filtered solution was shaken with 2 l. of ether and allowed to separate into two layers. For a further recovery of the oxidation products dissolved in the aqueous layer, alcohol was added until the greater portion of inorganic salts separated out from the solution, and the filtered solution was then neutralised with alkali, evaporated to dryness, acidified with hydrochloric acid, and extracted with 300 c.c. of ether. The ethereal solutions were united and the ether distilled off. The residue was extracted three times with petroleum ether, using 150 c.c. for each extraction, and separated into petroleum ether soluble portion (**B**) and petroleum ether insoluble portion (**C**). The three portions thus obtained were examined separately.

(i) *Oily portion* (**A**). Yield 10.5 g. This portion contained neutral substance which escaped oxidation, besides acidic substance. Sodium carbonate solution was added to this portion, and the resulting soap solution was treated with ether, by which 2.5 g. of neutral substance was obtained from the ethereal extract. The soap solution yielded on acidification an oily liquid having neutr. value 338.5 and saponif. value 691.6 (calc. for methyl hydrogen adipate $C_7H_{12}O_4$: neutr. value 350.5 and saponif. value 700.9). The free acid obtained on saponification followed by acidification consisted of a crystalline solid which crystallised from ethyl acetate in needles; neutr. value 767.1 (calc. for adipic acid $C_6H_{10}O_4$: 768.2), m.p. 152.5–153°, which was unaltered when admixed with an authentic specimen of adipic acid (Found: C, 49.09; H, 6.95. Calc. for $C_6H_{10}O_4$: C, 49.29; H, 6.90%).

(ii) *Petroleum ether soluble portion* (**B**). The petroleum ether solution was heated on the water-bath until the petroleum ether was driven off, and then the residue (2.8 g.) heated in an oil-bath. About 1 g. of a colourless liquid distilled before the temperature of the bath reached 150°, beyond which nearly nothing distilled out; and when the temperature of the bath reached about 210°, the residue showed an indication of decomposition. The petroleum ether which distilled first showed acid reaction. On neutralising it with barium hydroxide solution, it precipitated barium acetate (Found: Ba, 53.66. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The distillate boiling below 150° (temperature of bath) was found to consist of acetic acid, since silver acetate was obtained by neutralising with sodium hydroxide and then adding silver nitrate (Found: Ag, 64.59. Calc. for $C_2H_3O_2Ag$: Ag, 64.64%).

(iii) *Petroleum ether insoluble portion* (**C**). Yield 12.8 g. This portion consisted of a crystalline solid, and on recrystallisation from ethyl acetate it gave succinic acid; neutr. value 948.6 (calc. 950.6), m.p. and mixed m.p. 182.5–183° (Found: C, 40.60; H, 5.22. Calc. for $C_4H_6O_4$: C, 40.66; H, 5.12%). It is considered that this portion consists almost exclusively of succinic acid, and its yield is about 64% of the methyl hiragonate used for the oxidation. This is considerably higher than the theoretical yield of succinic acid, 44.68%, with the assumption that methyl hiragonate has only one $=CH\cdot(CH_2)_2\cdot CH=$ group.

3. Ozonolysis of Methyl Hiragonate. Methyl hiragonate (5 g.) was dissolved in chloroform (50 c.c.), and on cooling with ice-salt, a current of ozonised oxygen was passed through the solution until it became saturated. On distilling off the solvent under reduced pressure, the ozonide remained as a light yellow sirup. Twenty g. of methyl hiragonate yielded 32.2 g. of ozonide (161.0%). The yield calculated for normal ozonide $C_{17}H_{28}O_{11}$ and ozonide peroxide $C_{17}H_{28}O_{12}$ are 154.5 and 160.6%, respectively. The ozonide obtained here is probably ozonide peroxide. Water (200 c.c.) was added to the ozonide, and the liquid was heated in a flask on the water-bath for 30 minutes, a gentle current of hydrogen being passed into the flask. In order to recover the volatile decomposition products (**A**) which were carried over with hydrogen, the flask was attached by a delivery tube to other three flasks which were connected in succession, the first (**a**) being filled with 200 c.c. of water and cooled with ice, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The liquid remained in the initial flask consisted of aqueous solution and reddish orange oil ($\mathbf{B_1}$) which separated on the bottom of the flask. These were separated, and the clear aqueous solution was extracted with 2 l. of ether. After distilling off ether from the ethereal solution, 50 c.c. of water was added to the residue, of which a portion remained undissolved as an orange yellow oil ($\mathbf{B_2}$), and was separated from the aqueous solution (**C**). By these treatments, the decomposition products of ozonide were separated into (i) volatile substance (**A**), (ii) oily substance ($\mathbf{B_1}$ and $\mathbf{B_2}$) and (iii) the portion dissolved in water (**C**).

(i) *Volatile substance* (**A**). The aqueous solution of volatile substance collected in the flask (**a**) produced a pink colouration with Schiff's reagent, and a deep blue colouration with diethylamine and sodium nitroprusside, indicating that acetaldehyde is present in the aqueous solution. On adding *p*-nitrophenylhydrazine in hydrochloric acid, *p*-nitrophenylhydrazone of acetaldehyde separated, which crystallised from 50% alcohol in yellow needles; m.p. 126.5–127°, which was not lowered when admixed with a pure specimen, m.p. 127.5–128° (Found: N, 23.23. Calc. for $C_8H_9O_2N_3$: N, 23.46%). The aqueous solution showed also acid reaction, and gave a deep red colouration on adding ferric chloride after neutralisation. The barium salt, obtained from the solution by neutralisation with barium hydroxide, was found to be barium acetate (Found: Ba, 53.50. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%).

The barium hydroxide solution in the flask (**b**) was found to contain a small quantity of precipitate of barium carbonate (0.1528 g.), which indicated the formation of carbon dioxide by the decomposition of ozonide. But the yield of carbon dioxide calculated from the quantity of precipitated barium carbonate is only 0.17% of the methyl hiragonate used for ozonolysis. If a highly unsaturated acid having the $=CH\cdot CH_2\cdot CH=$ group is subjected to ozonolysis, carbon dioxide is formed by secondary decomposition of the oxidation products derived from that group thus: $HOOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COOH + CO_2$ and $HOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COH + CO_2$. It is, however, found from the results of our experiments which will be reported later that the secondary decomposition takes place to a considerable extent, though not to a quantitative extent, and it never gives such a small yield of carbon dioxide. Consequently, the formation of carbon dioxide in such a minute amount as in the case of above experiment gives an indication of the absence of the $=CH\cdot CH_2\cdot CH=$ group in methyl hiragonate; it is probably due either to the contamination of highly unsaturated acids having the $=CH\cdot CH_2\cdot CH=$ group or to an abnormal decomposition of a small portion of the ozonide of methyl hiragonate.

(ii) *Oily substance* (B_1 and B_2). Yield 10.9 g. It was separated into neutral and acidic portions by adding sodium hydroxide solution and extracting the resulting soap solution with ether. The neutral portion (2.4 g.) obtained from the ethereal solution had saponif. value 379.0 (calc. for semi-aldehyde of methyl hydrogen adipate $C_7H_{12}O_3$: 389.4). This was saponified and then oxidised with potassium permanganate in alkaline solution. The crystalline products obtained on acidification yielded pure adipic acid after recrystallising from ethyl acetate; neutr. value 766.8 (calc. for $C_6H_{10}O_4$: 768.2), m.p. and mixed m.p. 152–153°.

The acidic portion (8.5 g.) which was obtained from the soap solution on acidification and was collected by using ether, had neutr. value 340.0 and saponif. value 690.2 which are close to the corresponding values for methyl hydrogen adipate (neutr. value 350.5 and saponif. value 700.9). Adipic acid liberated from the ester in the usual way showed neutr. value 767.0 and m.p. 152–153° after recrystallising from ethyl acetate (Found: C, 49.16; H, 6.91. Calc. for $C_6H_{10}O_4$: C, 49.29; H, 6.90%).

(iii) *The portion dissolved in water* (C). Sodium carbonate solution was added to the aqueous solution of this portion, and the resulting soap solution was shaken with 2 l. of ether and allowed to separate into two layers. After removal of the ether from the ethereal solution, there remained 1.2 g. of neutral substance (C_1). The soap solution was decomposed with hydrochloric acid, extracted with 2 l. of ether, and on distilling off the ether from ethereal extract, 17 g. of acidic substance (C_2) was obtained.

The neutral substance (C_1) showed aldehyde reaction. It was subjected to a further oxidation with alkaline permanganate solution, and the product, which after acidification was collected by using ether, was treated with a little water in which a portion remained undissolved. The insoluble portion had neutr. value 342.6 and saponif. value 691.2 (calc. for methyl hydrogen adipate: neutr. value 350.5 and saponif. value 700.9), and the free acid obtained on acidification of the saponified product melted at 149–150° and was considered to be an impure adipic acid. The aqueous extract on evaporation left behind a crystalline solid which melted at 175°, and it was likely to be an impure succinic acid. From these experiments, it is seen that the neutral substance (C_1) contains semi-aldehyde of methyl hydrogen adipate and succinic aldehyde (or its polymerised products).

The acidic substance (C_2) was extracted three times with petroleum ether, using 150 c.c. for each extraction. The united petroleum ether solution was heated on the water-bath to remove petroleum ether. The distilled petroleum ether showed an acid reaction and had an odour of acetic acid. The barium salt, obtained on neutralising the petroleum ether with barium hydroxide, was found to consist of barium acetate (Found: Ba, 53.60. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). After distilling off petroleum ether, the residue (2 g.) was heated in an oil-bath, and a small quantity of distillate was obtained before the temperature of oil-bath reached 150°. Beyond 150°, practically nothing distilled over, and when the temperature of bath reached about 200°, the distillation was stopped since there were the indications of decomposition. The silver salt, prepared from the distillate by neutralising with sodium hydroxide and adding silver nitrate, was found to consist of silver acetate (Found: Ag, 64.50. Calc. for $C_2H_3O_2Ag$: Ag, 64.64%). The final residue from distillation was oxidised with alkaline permanganate solution, and the product obtained after acidification was found to be an impure succinic acid, m.p. 177–177.5°.

The petroleum ether insoluble portion (14.5 g.) consisted of a mixture of crystalline solid and liquid. It was oxidised with alkaline permanganate solution, and the product obtained after acidification was recrystallised from ethyl acetate to yield succinic acid; neutr. value 948·7, m.p. 182.5–183° (Found: C, 40·61; H, 5·10. Calc. for $C_4H_6O_4$: C, 40.66; H, 5.12%). Twenty g. of methyl hiragonate gave 14.5 g. or 72.5% yield of petroleum ether insoluble portion. Since it is considered that the petroleum ether insoluble portion consists almost entirely of succinic acid and its semi-aldehyde, methyl hiragonate should have two $=CH\cdot(CH_2)_2\cdot CH=$ group. (The maximum yield of succinic acid will be 44.68% if it has only one of such group.)

Summary.

Methyl hiragonate has been prepared from Japanese sardine oil, and it was subjected to the oxidation by the permanganate method and by the ozonide method. Among the oxidation products obtained by the permanganate method, succinic acid, acetic acid and methyl hydrogen adipate were identified. The products obtained by the ozonide method contained, besides the above-mentioned three acidic compounds, acetaldehyde and semi-aldehyde of methyl hydrogen adipate, and also the presence of semi-aldehyde of succinic acid and succinic aldehyde (or its polymerised products) was indicated. Accordingly, the constitution of hiragonic acid is $\Delta^{6:7,\ 10:11,\ 14:15}$-hexadecatrienoic acid : s expressed by the following formula :

$$CH_3\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_4\cdot COOH$$

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HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. XIII.* REACTIONS BETWEEN HYDROGEN AND SOLID INORGANIC COMPOUNDS.

By Susumu MIYAMOTO.

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Investigations on the reduction of a number of solid inorganic substances by hydrogen under the silent electric discharge were carried out;

* Heterogeneous chemical reactions in the silent electric discharge. XII; *Kolloid-Z.*, **69** (1934), 179.

there follows an account of the results obtained since the publication of the previous papers.[1] The apparatus and the method of investigation are essentially the same as those mentioned in the previous papers.[1]

(1) **Selenious acid.** The quantity of selenious acid, H_2SeO_3, employed = 2 g. Time of silent electric discharge = 2 hours. The white powder became yellowish red soon after the electric current was passed, and the wall of the discharge tube was gradually covered with a thin yellow film of metallic selenium.

The reaction product was dissolved in water; red metallic selenium remained. The formation of a thin metallic film on the wall of the discharge tube suggests that hydrogen selenide is produced first, and the reactions in the discharge tube seem to be expressed by the following equations:

$$H_2SeO_3 + 3H_2 = Se_2H_2 + 3H_2O,$$
$$SeH_2 = Se + H_2.$$

(2) **Selenic acid.** Selenic acid, H_2SeO_4, employed = 2 g. Time of silent electric discharge = 2 hours. As selenic acid is an extremely hygroscopic compound, it had absorbed a small quantity of water, which was not determined. The white powder became red, showing the liberation of metallic selenium. The reduction products were shaken with water, and filtered. Red powder of metallic selenium remained. The presence of selenious acid in the filtrate was proved in the normal manner.[2]

The reaction products are selenious acid and metallic selenium, and the reactions in the discharge tube are expressed by the following equations:

$$H_2SeO_4(\text{solid}) + H_2 = H_2SeO_3 + H_2O,$$
$$H_2SeO_3 + 2H_2 = Se + 3H_2O.$$

(3) **Sodium selenate.** Sodium selenate, $Na_2SeO_4 \cdot 10H_2O$, employed = 3 g. Time of silent electric discharge = 3 hours. The powder became red, showing the liberation of metallic selenium. Water was added to the discharge tube, well shaken and filtered. Red metallic selenium remained. The presence of selenite in the filtrate was proved quite the same way as in the case of selenic acid.

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(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320.

(2) Treadwell-Hall, "Analytical Chemistry", 8th Edition, Vol. I, p. 541.

The principal reaction products are selenite and metallic selenium, and the reactions in the discharge tube are expressed by the following equations:

$$Na_2SeO_4(solid) + H_2 = Na_2SeO_3 + H_2O,$$
$$Na_2SeO_3 + 2H_2 = Se + 2NaOH + H_2O.$$

(4) **Tellurous acid.** Tellurous acid, H_2TeO_3, employed = 2 g. Time of silent electric discharge = 2 hours. Not only the white powder became black, but the wall of the discharge tube was also covered with a thin film of metallic tellurium, forming a beautiful mirror.

The formation of tellurium mirror suggests that hydrogen telluride is first produced, and the reactions in the discharge tube are expressed by

$$H_2TeO_3(solid) + 3H_2 = TeH_2 + 3H_2O,$$
$$TeH_2 = Te + H_2.$$

It is an interesting fact that when selenious or tellurous acid is reduced under the silent electric discharge, metallic hydride is first produced, quite in the same way as in the case of the reduction of arsenic[3] or antimony compounds.[4]

(5) **Sodium tellurite.** Sodium tellurite, Na_2TeO_3, employed = 2 g. Time of silent electric discharge = 4 hours. White powder became black soon after the electric current was passed, showing the liberation of metallic tellurium. In this case no appreciable amount of metallic tellurium was deposited on the wall of the discharge tube. The reaction in the discharge tube is expressed by

$$Na_2TeO_3(solid) + 2H_2 = Te + 2NaOH + H_2O.$$

(6) **Telluric acid.** Telluric acid, $H_2TeO_4 2H_2O$, employed = 3 g. Time of silent electric discharge = 4 hours. White powder became black soon after the electric current was passed, and the wall of the discharge tube was gradually covered with a thin film of metallic tellurium.

Alkaline solution was added to the discharge tube, well shaken, and filtered. Metallic tellurium remained. The filtrate contained tellurite.[5] The principal reaction products are tellurous acid and metallic tellurium, and the reactions in the discharge tube seem to be expressed by

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(3) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 734, 735.
(4) *Ibid.*, **53** (1932), 789, 790, 791.
(5) Treadwell-Hall, "Analytical Chemistry", 8th Edition, Vol. I., p. 545.

$$H_2TeO_4(solid) + H_2 = H_2TeO_3 + H_2O,$$
$$H_2TeO_3 + 3H_2 = TeH_2 + 3H_2O,$$
$$TeH_2 = Te + H_2.$$

(7) Potassium thiosulphate. Exp. 1. The production of potassium sulphate, hydrogen sulphide, and sulphur was proved quite in the same way as in the case of sodium thiosulphate.[6]

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of potassium thiosulphate employed = 7.0 g. Time of silent electric discharge = 7 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.82 c.c.

It seems that the principal reactions in the discharge tube are expressed by the following equations:

$$K_2S_2O_3 + H_2 = K_2SO_3 + H_2S,$$
$$4K_2S_2O_3 = 3K_2SO_4 + K_2S_5,$$
$$K_2S_5 = K_2S + 4S,$$
$$K_2S + 2H_2O = 2KOH + H_2S,$$
$$S + H_2 = H_2S.$$[7]

(8) Silver carbonate. Silver carbonate, Ag_2CO_3, employed = 2 g. Time of silent electric discharge=4 hours. On leaving the discharge tube the gas was passed through an absorption bottle, containing barium hydroxide solution.

Soon after the electric current was passed, the powder in the discharge tube became black, and in the absorption bottle white precipitate was produced, showing the production of metallic silver and carbon dioxide. The reaction products in the discharge tube were shaken with hot dilute sulphuric acid to dissolve silver carbonate remained and silver oxide produced. A small quantity of white powder remained. On rubbing the powder with a glass rod, it manifested metallic lustre, showing that it is metallic silver.

The principal reactions in the discharge tube are expressed by

$$Ag_2CO_3(solid) = Ag_2O + CO_2,$$
$$Ag_2O + H_2 = 2Ag + H_2O.$$[8]

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(6) S. Miyamoto, *J. Chem. Soc. Japan*, **55** (1934), 1145.
(7) *Ibid.*, **53**
(8) *Ibid.*, **53** (1932), 796.

According to Losanitsch,[9] the following reaction is also possible in the present case.

$$CO_2 + H_2 = HCOOH.$$

(9) **Lithium chlorate.** Exp. 1. The formation of lithium chloride was proved quite in the same way as in the case of potassium chlorate.[10]

Exp. 2. The quantity of lithium chloride produced was determined by Volhard's method.[11] Lithium chlorate, $LiClO_3 \cdot \frac{1}{2} H_2O$, employed = 7.0 g. Time of silent electric discharge = 6 hours. Volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of lithium chloride produced = 26.10 c.c.

The reaction in the discharge tube is expressed by

$$LiClO_3(\text{solid}) + 3H_2 = LiCl + 3H_2O.$$

(10) **Sodium bromate.** Exp. 1. Sodium bromate, $NaBrO_3$, employed =4 g. Time of silent electric discharge = 6 hours. No appreciable change was observed in the appearance of the powder.

The reaction product was dissolved in water and the solution was acidified with dilute sulphuric acid. The solution became yellow and it decolourizes methylorange, showing the liberation of free bromine:

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

It proves the formation of potassium bromide in the the discharge tube.

Exp. 2. The quantity of sodium bromide produced was calculated by the determination of the quantity of sodium bromate remained. Sodium bromate employed = 6.1851 g. Time of silent electric discharge = 5 hours. Volume of arsenious acid solution of 0.1000 normal, equivalent to the quantity of sodium bromide produced = 58.5 c.c.

The reaction in the discharge tube is expressed by

$$NaBrO_3(\text{solid}) + 3H_2 = NaBr + 3H_2O.$$

Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacts with the following inorganic solid substances.

(9) *Ber.*, **30** (1897), 135.
(10) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 731.
(11) Treadwell-Hall, "Analytical Chemistry", 7th Edition, Vol. II, p. 603.

	Reacting substance	Reaction products
(1)	Selenious acid	Selenium
(2)	Selenic acid	Selenium and selenious acid
(3)	Sodium selenate	Selenium and sodium selenite
(4)	Tellurous acid	Tellurium
(5)	Sodium tellurite	Tellurium and sodium hydroxide
(6)	Telluric acid	Tellurium and tellurous acid
(7)	Potassium thiosulphate	Potassium sulphite, hydrogen sulphide, and sulphur
(8)	Silver carbonate	Silver and carbon dioxide
(9)	Lithium chlorate	Lithium chloride
(10)	Sodium bromate	Sodium bromide

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DIE KONZENTRATION DER SCHWEREN ISOTOPE IN KOHLENHYDRATEN.

(Vorläufige Mitteilung.)

Von Toshizo TITANI und Masao HARADA.

Eingegangen am 15. April, 1935. Ausgegeben am 28. Mai, 1935.

Früher[1] haben wir gefunden, dass das Wasser aus der Rohrzuckermelasse um 2.8 γ schwerer als gewöhnliches Wasser ist. Dies hat uns veranlasst das aus dem Zucker selbst durch Verbrennung erhaltene Wasser zu untersuchen. Es wurde dabei gefunden, dass das Wasser aus dem gereinigten Rohrzucker um 7.4 γ und das aus dem Rübenzucker um 6.5 γ schwerer als das Osaka-Leitungswasser waren. Weil dies nun die Vermutung nahe legte, dass eine Anreicherung von schweren Isotopen in allen Kohlenhydraten allgemein vorhanden ist, untersuchten wir möglichst viele Sorten von Substanzen, die Kohlenhydrate als Hauptbestandteil enthalten, nach ihren Gehalt an schweren Isotopen. Die Substanzen wurden direkt im Luftstrom verbrannt, das dabei erhaltene Wasser wurde sorgfältig gereinigt und sein spezifisches Gewicht bei 8°C. mit dem ebenso gereinigten Osaka-Leitungswasser verglichen. Wir fanden dabei, wie erwartet, dass das Probewasser aus den Substanzen, die Glukose, Laktose, Stärke, Dextrin, Galaktan, Mannan und Zellulose als Hauptbestandteil enthalten, durchschnittlich um 6 γ schwerer als das Normalwasser waren. Die Einzelheiten sollen später in diesem Bulletin berichtet werden.

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(1) Vgl. T. Titani und M. Harada, dies Bulletin, **10** (1935), 31.

ISOTOPENZUSAMMENSETZUNG DES REGEN- UND SCHNEEWASSERS.

(Vorläufige Mitteilung.)

Von Masao HARADA und Toshizo TITANI.

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Während des Versuchs über den Deuterium-Gehalt von Wasserproben in verschiedenen natürlichen Vorkommen, fanden wir kleine, aber untrügliche Schwankungen in der Dichte des Regenwassers. Nach einigen Versuchen überzeugten wir uns, dass das Regenwasser, am Anfang eines Regenfalls immer schwerer als gewöhnliches Bodenwasser ist und gegen Ende allmählich leichter wird. Wir sammelten z.B. bei einem Regenfall das Wasser separat in drei Mengen. Die Anfangsmenge, deren Volumen 340 c.c. betrug, erwies sich um 1.6 γ schwerer als das Normalwasser. Dagegen fanden wir, dass die mittlere Menge, deren Volumen 1180 c.c. betrug, um 1.3 γ leichter und die letzte Menge von 30 c.c. um 1.9 γ leichter als das Normalwasser waren. Diese Ergebnisse kann man vielleicht entweder durch die fraktionierte Kondensation oder durch Verdampfung erklären.

Das Schneewasser, das wir dann untersuchten, erwies sich ausnahmslos leichter als das Normalwasser. Der grösste Unterschied, den wir bisher gefunden haben, betrug sogar 3.3 γ und der kleinste 0.5 γ, durchschnittlich etwa 2 γ. Die Erklärung für diese Ergebnisse kann man vielleicht darin finden, dass die Feuchtigkeit in der Atmosphäre sich unter den Wirkung der Gravitationskraft befindet. Die Einzelheiten sollen später in diesem Bulletin berichtet werden.

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